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(54) Polyethylene composition for pressure pipes with enhanced flexibility

Multimodale Polyethylenzusammensetzung für Rohre mit erhöhter Flexibilität

Composition de polyéthylène multimodal pour tuyaux avec flexibilité

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Description

[0001] The present invention relates to a pipe comprising a polyethylene composition comprising a polymeric base resin comprising two polyethylene fractions with different molecular weight. Furthermore, the present invention relates to the use of said composition for the production of a pipe.

[0002] Polyethylene compositions comprising two or more polyethylene fractions with different molecular weight are often referred to as bimodal or multimodal polyethylene compositions. Such polyethylene compositions are frequently used e.g. for the production of pipes due to their favourable physical and chemical properties as e.g. mechanical strength, corrosion resistance and long-term stability. When considering that the fluids, such as water or natural gas, transported in a pipe often are pressurized and have varying temperatures, usually within a range of 0 °C to 50 °C, it is obvious that the polyethylene composition used for pipes must meet demanding requirements. On the other hand, to facilitate installation of the pipes e.g. into the ground, a high flexibility of the pipes is desired.

[0003] In particular, the polyethylene composition used for a pipe should have high mechanical strength, good long-term stability, notch/creep resistance and crack propagation resistance, and, at the same time high flexibility. However, at least some of these properties are contrary to each other so that it is difficult to provide a composition for pipes which excels in all of these properties simultaneously. For example, stiffness imparting mechanical strength to the pipe is known to improve with higher density but, in contrast, flexibility and notch/creep resistance is known to improve with reduced density.

[0004] Furthermore, as polymer pipes generally are manufactured by extrusion, or, to a smaller extent, by injection moulding, the polyethylene composition also must have good processability.

[0005] It is known that in order to comply with the contrary requirements for a pipe material, bimodal polyethylene compositions may be used. Such compositions are described e.g. in EP 0 739 937 and WO 02/102891. The bimodal polyethylene compositions described in these documents usually comprise two polyethylene fractions, wherein one of these two fractions has a lower molecular weight than the other fraction and is preferably a homopolymer, the other fraction with higher molecular weight preferably being an ethylene copolymer comprising one or more alpha-olefin comonomers.

[0006] One great disadvantage of such pipes when used for gas or cold water infrastructure is the lack of flexibility of the pipes. The pipes are rigid and strong. These mechanical properties are the result of the high demands regarding mechanical strength and long-term stability.

[0007] In laying known gas or cold water pipes, for example in open-trench laying or trenchless laying technologies like plough-in-place laying, often problems occur due to the stiffness of the pipes. It is often difficult to align and manoeuvre the pipes into the trenches. Still further, it is often a problem to straighten pipes which are stored or transported as coils. The same problem occurs if bends have to be passed which is particularly important for pipes of smaller and medium size. All these problems are of course even more relevant when the stiffness of the pipes increases due to lower temperature, for example in cold weather.

[0008] It is thus particularly desirable to provide a pipe with enhanced flexibility without loosing the mechanical strength and the long term stability.

[0009] Accordingly, it is the object of the present invention to provide a pipe comprising a polyethylene composition having an improved combination of properties, in particular having enhanced flexibility and, simultaneously, high mechanical strength and good long-term stability.

[0010] The present invention is based on the surprising finding that the above mentioned object can be achieved by a pipe comprising a polyethylene composition comprising at least two polymer fractions with different molecular weights, having carefully selected values of density and MFR_5 within small ranges and the polyethylene composition having a shear stress in a particular range.

[0011] Accordingly, the present invention provides a pipe comprising a polyethylene composition comprising a base resin which comprises

(a) an ethylene homo- or copolymer fraction (A); and

(b) an ethylene homo- or copolymer fraction (B),

wherein

(i) fraction (A) has a lower weight average molecular weight than fraction (B);

(ii) the base resin has a density of 932 to 938 kg/m^3;

(ii) the polyethylene composition has an MFR_5 of 0.1 to 0.6 g/10 min ; and

(iv) the polyethylene composition has a shear stress $\eta_{2.7\,kPa}$ of 85 to 230 kPas.

[0012] It has been found that with such polyethylene compositions pipes can be produced which have an enhanced flexibility. Therefore, pipes made of this polyethylene composition can more easily be straightened, aligned into the trenches and passed around comers. Nevertheless, such pipes have also high mechanical strength, which e.g. allows for the pipe being used for the transport of pressurized fluids, an excellent long-term stability and a good rapid crack propagation resistance. Furthermore, the polyethylene compositions also have good processability.

[0013] It should be noted that the pipe of the present invention is characterised not by any single one of the above defined features, but by their combination. By this unique combination of features it is possible to obtain pipes of superior performance, particularly with regard to flexibility and rapid crack propagation (RCP), while minimum required strength (MRS), processability, impact strength and slow crack propagation resistance are maintained.

[0014] The term molecular weight where used herein denotes the weight average molecular weight M_w.

[0015] The term "base resin" denotes the entirety of polymeric components in the polyethylene composition according to the invention, usually making up at least 90 wt% of the total composition. Preferably, the base resin is consisting of fractions (A) and (B), optionally further comprising a prepolymer fraction in an amount of up to 20 wt%, preferably up to 10 wt%, more preferably up to 5 wt% of the total base resin.

[0016] In addition to the base resin, usual additives for utilization with polyolefins, such as pigments, stabilizers (antioxidant agents), antacids and/or anti-UVs, antistatic agents and utilization agents (such as processing aid agents) may be present in the polyethylene composition. Preferably, the amount of these additives is 10 wt% or below, further preferred 8 wt% or below, still more preferred 4 wt% or below of the total composition.

[0017] Preferably, the composition comprises carbon black in an amount of 8 wt% or below, further preferred of 1 to 4 wt%, of the total composition.

[0018] Further preferred, the amount of additives different from carbon black is 1.5 wt% or less, more preferably 1.0 wt% or less, most preferably 0.5 wt% or less.

[0019] Usually, a polyethylene composition such as that used in the present invention, comprising at least two polyethylene fractions, which have been produced under different polymerisation conditions resulting in different weight average molecular weights for the fractions, is referred to as "multimodal". The prefix "multi" relates to the number of different polymer fractions the composition is consisting of. Thus, for example, a composition consisting of two fractions only is called "bimodal".

[0020] The form of the molecular weight distribution curve, i.e. the appearance of the graph of the polymer weight fraction as function of its molecular weight, of such a multimodal polyethylene will show two or more maxima or at least be distinctly broadened in comparison with the curves for the individual fractions.

[0021] For example, if a polymer is produced in a sequential multistage process, utilising reactors coupled in series and using different conditions in each reactor, the polymer fractions produced in the different reactors will each have their own molecular weight distribution and weight average molecular weight. When the molecular weight distribution curve of such a polymer is recorded, the individual curves from these fractions are superimposed into the molecular weight distribution curve for the total resulting polymer product, usually yielding a curve with two or more distinct maxima.

[0022] The polyethylene composition preferably has an MFR_5 of 0.15 to 0.5 g/10 min, more preferably of 0.2 to 0.45 g/10 min.

[0023] The base resin preferably has a density of 933 to 937 kg/m^3.

[0024] The shear stress $\eta_{2.7\,kPa}$ of the polyethylene composition is preferably 95 to 210 kPas and more preferably 100 to 200 kPas.

[0025] In a preferred embodiment the polyethylene composition further comprises a nucleating agent. The amount of such a nucleating agent in the polyethylene composition is preferably 0.01 to 0.5 wt%, further preferred 0.05 to 0.25 wt%.

[0026] The nucleating agent may be any compound or mixture of compounds capable of nucleating the crystallization, such as a pigment having a nucleating effect or an additive used only for nucleating purposes. Examples of the first category of compounds are phtalocyanine blue or green pigments (e.g. PB15:1, PB15:3, PG7), isoindolinone and isoindoline pigments (e.g. PY109, PY110, P061), benzimidazolone pigments (e.g. P062, P072), quinacridone pigments (e.g. PY19), benzimidazolone pigments (e.g. PY180, PY181), quinophtalone pigments (e.g. PY138), chinacridone pigments (e.g. Pigment Violet PV19) and azoheterocyclus pigments (e.g. P064).

[0027] The nucleating agent may also be a polymeric additive, such as a polymer of vinylcyclohexane or 3-methyl-1-butene. In such case, the polymeric additive, which preferably has a melting point above 200 °C, may be blended into the bimodal polymer by conventional means in an extruder, or it may be prepolymerized on the catalyst as disclosed e.g. in WO 99/24478.

[0028] Fraction (A) preferably has a MFR_2 of 10 to 400 g/10 min, more preferably of 20 to 200 g/10 min, still more preferably of 25 to 100 g/10 min.

[0029] Fraction (A) preferably has a density of 960 to 980 kg/m^3.

[0030] The SHI is the ratio of the viscosity of the polyethylene composition at different shear stresses. In the present

invention, the shear stresses at 2.7 kPa and 210 kPa are used for calculating the $SHI_{(2.7/210)}$ which may serve as a measure of the broadness of the molecular weight distribution.

[0031] The SHI of the polyethylene compositions used in the present invention is comparatively low. This is an indication of a rather narrow molecular weight distribution of the base resin. The SHI of the polyethylene compositions is preferably 10 to 49, more preferably 10 to 45 and still more preferably 15 to 35.

[0032] Furthermore, fraction (A) preferably is an ethylene homopolymer.

[0033] The flexural modulus of the polyethylene composition is preferably 300 to 700 MPa, more preferably 400 to 700 MPa.

[0034] The weight split in the base resin between fraction (A) and fraction (B) is preferably (30-47) : (70-53), more preferably (35-45) : (65-55).

[0035] Furthermore, the polyethylene composition has a good rapid crack propagation resistance. A pipe made of the multimodal polyethylene composition preferably has a ductile brittleness temperature ($T_{crit.}$) of -6 °C or lower, more preferably -8 °C or lower (RCP-S4 value).

[0036] Still further, the polyethylene composition has a slow crack propagation resistance of at least 500 h, more preferably of at least 1000 h, still more preferably of at least 1500 h, and most preferably of at least 2000 h at 4.0 MPa hoop stress and 8.0 bar internal pressure at 80 °C.

[0037] A pressure pipe made of the multimodal polymer composition preferably has a design stress rating of at least MRS 8.0.

[0038] Preferably, the polyethylene compositions, without Carbon black or fillers, of the present invention fulfil the following relationship:

$$\frac{FM}{\ln\left(\frac{\eta_{747\,Pa}}{SHI_{2.7/210}} \times MFR_5\right)} \leq 800$$

wherein FM denotes the flexural modulus as described above.

[0039] The numerator of the above given formula defines the flexibility of the material. If the flexibility becomes too high, however, the material loses its ability to withstand pressure. The denominator defines the pressure resistance of the material. Therefore, the above given relationship shows how to find a polyethylene composition which fulfils both the demands of flexibility and pressure resistance.

[0040] The base resin of the polyethylene composition preferably comprises at least 0.2 mol%, more preferably at least 0.75 mol%, and still more preferably at least 0.95 mol% of at least one alpha-olefin comonomer. The amount of comonomer is preferably at most 3.0 mol%, more preferably at most 2.5 mol%, and still more preferably at most 2.0 mol%.

[0041] Fraction (B) of the polyethylene composition preferably comprises at least 0.4 mol%, more preferably at least 0.6 mol%, and still more preferably at least 0.8 mol% of at least one alpha-olefin comonomer. The amount of comonomer is preferably at most 6.0 mol%, more preferably at most 5.0 mol%, and still more preferably at most 4.0 mol%.

[0042] As an alpha-olefin comonomer, preferably an alpha-olefin having from 4 to 8 carbon atoms is used. Still more preferably an alpha-olefin selected from 1-butene, 1-hexene, 4-methyl-1-pentene and 1-octene is used.

[0043] Where herein features of fractions (A) and/or (B) of the composition are given, these values are generally valid for the cases in which they can be directly measured on the respective fraction, e.g. when the fraction is separately produced or produced in the first stage of a multistage process.

[0044] However, the base resin may also be and preferably is produced in a multistage process wherein e.g. fractions (A) and (B) are produced in subsequent stages. In such a case, the properties of the fractions produced in the second and third step (or further steps) of the multistage process can either be inferred from polymers, which are separately produced in a single stage by applying identical polymerisation conditions (e.g. identical temperature, partial pressures of the reactants/diluents, suspension medium, reaction time) with regard to the stage of the multistage process in which the fraction is produced, and by using a catalyst on which no previously produced polymer is present. Alternatively, the properties of the fractions produced in a higher stage of the multistage process may also be calculated, e.g. in accordance with B. Hagström, Conference on Polymer Processing (The Polymer Processing Society), Extended Abstracts and Final Programme, Gothenburg, August 19 to 21, 1997, 4:13.

[0045] Thus, although not directly measurable on the multistage process products, the properties of the fractions produced in higher stages of such a multistage process can be determined by applying either or both of the above methods. The skilled person will be able to select the appropriate method.

[0046] The polyethylene composition used in accordance with the invention preferably is produced so that at least one of fractions (A) and (B), preferably (B), is produced in a gas-phase reaction.

[0047] Further preferred, one of the fractions (A) and (B) of the polyethylene composition, preferably fraction (A), is

produced in a slurry reaction, preferably in a loop reactor, and one of the fractions (A) and (B), preferably fraction (B), is produced in a gas-phase reaction.

[0048] Further, the polyethylene base resin preferably is produced in a multistage process. Polymer compositions produced in such a process are also designated as "in-situ"-blends.

[0049] A multistage process is defined to be a polymerisation process in which a polymer comprising two or more fractions is produced by producing each or at least two polymer fraction(s) in a separate reaction stage, usually with different reaction conditions in each stage, in the presence of the reaction product of the previous stage which comprises a polymerisation catalyst.

[0050] Accordingly, it is preferred that fraction (A) and (B) of the polyethylene composition are produced in different stages of a multistage process.

[0051] Preferably, the multistage process comprises at least one gas phase stage in which, preferably, fraction (B) is produced.

[0052] Further preferred, fraction (B) is produced in a subsequent stage in the presence of fraction (A) which has been produced in a previous stage.

[0053] It is previously known to produce multimodal, in particular bimodal, olefin polymers, such as multimodal polyethylene, in a multistage process comprising two or more reactors connected in series. As instance of this prior art, mention may be made of EP 517 868, as a preferred multistage process for the production of the polyethylene composition.

[0054] Preferably, the main polymerisation stages of the multistage process are such as described in EP 517 868, i.e. the production of fractions (A) and (B) is carried out as a combination of slurry polymerisation for fraction (A)/gas-phase polymerisation for fraction (B). The slurry polymerisation is preferably performed in a so-called loop reactor. Further preferred, the slurry polymerisation stage precedes the gas phase stage.

[0055] Optionally and advantageously, the main polymerisation stages may be preceded by a prepolymerisation, in which case up to 20 wt%, preferably 1 to 10 wt%, more preferably 1 to 5 wt%, of the total base resin is produced. The prepolymer is preferably an ethylene homopolymer (HDPE). At the prepolymerisation, preferably all of the catalyst is charged into a loop reactor and the prepolymerisation is performed as a slurry polymerisation. Such a prepolymerisation leads to less fine particles being produced in the following reactors and to a more homogeneous product being obtained in the end.

[0056] The polymerisation catalysts include coordination catalysts of a transition metal, such as Ziegler-Natta (ZN), metallocenes, non-metallocenes, Cr-catalysts. The catalyst may be supported, e.g. with conventional supports including silica, Al-containing supports and magnesium dichloride based supports. Preferably the catalyst is a ZN catalyst, more preferably the catalyst is a non-silica supported ZN catalyst, and most preferably a $MgCl_2$-based ZN catalyst.

[0057] The Ziegler-Natta catalyst further preferably comprises a group 4 (group numbering according to new IUPAC system) metal compound, preferably titanium, magnesium dichloride and aluminium.

[0058] The catalyst may be commercially available or be produced in accordance or analogously to the literature. For the preparation of the preferable catalyst usable in the invention reference is made to WO2004055068 and WO2004055069 of Borealis and EP 0 810 235. Particularly preferred Ziegler-Natta catalysts are described in EP 0 810 235.

[0059] The resulting end product consists of an intimate mixture of the polymers from the reactors, the different molecular-weight-distribution curves of these polymers together forming a molecular-weight-distribution curve having a broad maximum or several maxima, i.e. the end product is a multimodal polymer mixture.

[0060] It is preferred that the multimodal base resin of the polyethylene composition is a bimodal polyethylene mixture consisting of fractions (A) and (B), optionally further comprising a small prepolymerisation fraction in the amount as described above. It is also preferred that this bimodal polymer mixture has been produced by polymerisation as described above under different polymerisation conditions in two or more polymerisation reactors connected in series. Owing to the flexibility with respect to reaction conditions thus obtained, it is most preferred that the polymerisation is carried out in a loop reactor/a gas-phase reactor combination.

[0061] Preferably, the polymerisation conditions in the preferred two-stage method are so chosen that the comparatively low-molecular polymer having no content of comonomer is produced in one stage, preferably the first stage, owing to a high content of chain-transfer agent (hydrogen gas), whereas the high-molecular polymer having a content of comonomer is produced in another stage, preferably the second stage. The order of these stages may, however, be reversed.

[0062] In the preferred embodiment of the polymerisation in a loop reactor followed by a gas-phase reactor, the polymerisation temperature in the loop reactor preferably is 85 to 115 °C, more preferably is 90 to 105 °C, and most preferably is 92 to 100 °C, and the temperature in the gas-phase reactor preferably is 70 to 105 °C, more preferably is 75 to 100 °C, and most preferably is 82 to 97 °C.

[0063] A chain-transfer agent, preferably hydrogen, is added as required to the reactors, and preferably 200 to 800 moles of H_2/kmoles of ethylene are added to the reactor, when the LMW fraction is produced in this reactor, and 0 to 50 moles of H_2/kmoles of ethylene are added to the gas phase reactor when this reactor is producing the HMW fraction.

[0064] The composition preferably is produced in a process comprising a compounding step, wherein the composition

of the base resin, i.e. the blend, which is typically obtained as a base resin powder from the reactor, is extruded in an extruder and then pelletised to polymer pellets in a manner known in the art.

[0065] Optionally, additives or other polymer components can be added to the composition during the compounding step in the amount as described above. Preferably, the composition obtained from the reactor is compounded in the extruder together with additives in a manner known in the art.

[0066] The extruder may be e.g. any conventionally used extruder.

[0067] Furthermore, the present invention relates to a pipe comprising a polyethylene composition as described above and to the use of such a polyethylene composition for the production of a pipe.

Examples

1. Definitions and measurement methods

a) Density

[0068] Density is measured according to ISO 1183-2. Sample preparation is done in accordance with ISO 1872-2B.

b) Melt Flow Rate/Flow Rate Ratio

[0069] The melt flow rate (MFR) is determined according to ISO 1133 and is indicated in g/10 min. The MFR is an indication of the flowability, and hence the processability, of the polymer. The higher the melt flow rate, the lower the viscosity of the polymer. The MFR is determined at 190 °C and may be determined at different loadings such as 2.16 kg (MFR_2), 5.00 kg (MFR_5) or 21.6 kg (MFR_{21}).

[0070] The quantity FRR (flow rate ratio) is an indication of molecular weight distribution and denotes the ratio of flow rates at different loadings. Thus, $FRR_{21/5}$ denotes the value of MFR_{21}/MFR_5.

c) Rheological parameters

[0071] Rheological parameters such as Shear Thinning Index SHI and Viscosity are determined by using a rheometer, preferably a Physica MCR 300 Rheometer distributed by Anton Paar GmbH. The definition and measurement conditions are described in detail on page 8 line 29 to page 11, line 25 of WO 00/22040.

d) Rapid crack propagation

[0072] The rapid crack propagation (RCP) resistance of a pipe is determined according to a method called the S4 test (Small Scale Steady State), which has been developed at Imperial College, London, and which is described in ISO 13477:1997 (E).

[0073] According to the RCP-S4 test a pipe is tested, which has an axial length not below 7 pipe diameters. The outer diameter of the pipe is about 110 mm or greater and its wall thickness about 10 mm or greater. When determining the RCP properties of a pipe in connection with the present invention, the outer diameter and the wall thickness have been selected to be 110 mm and 10 mm, respectively. While the exterior of the pipe is at ambient pressure (atmospheric pressure), the pipe is pressurised internally, and the internal pressure in the pipe is kept constant at a pressure of 0.5 MPa positive pressure. The pipe and the equipment surrounding it are thermostatted to a predetermined temperature. A number of discs have been mounted on a shaft inside the pipe to prevent decompression during the tests. A knife projectile is shot, with well-defined forms, towards the pipe close to its one end in the so-called initiating zone in order to start a rapidly running axial crack. The initiating zone is provided with an abutment for avoiding unnecessary deformation of the pipe. The test equipment is adjusted in such a manner that crack initiation takes place in the material involved, and a number of tests are effected at varying temperatures. The axial crack length in the measuring zone, having a total length of 4.5 diameters, is measured for each test and is plotted against the set test temperature. If the crack length exceeds 4 diameters, the crack is assessed to propagate. If the pipe passes the test at a given temperature, the temperature is lowered successively until a temperature is reached, at which the pipe no longer passes the test, but the crack propagation exceeds 4 times the pipe diameter. The critical temperature (T_{crit}), i.e. the ductile brittle transition temperature as measured according to ISO 13477:1997 (E) is the lowest temperature at which the pipe passes the test. The lower the critical temperature the better, since it results in an extension of the applicability of the pipe.

e) Notch test

[0074] The slow crack propagation resistance is determined according to ISO 13479:1997 in terms of the number of

hours the pipe withstands a certain pressure at a certain temperature in the Notch test before failure. Pipes with a diameter of 110 mm are used. Herein, a pressure of 8.0 bars and a temperature of 80 °C have been used to obtain an aimed stress of 4.0 MPa. The measurement is made on a 110 SDR 11 pipe.

f) Constant Tensile Load (CTL)

[0075] The slow crack propagation resistance is determined with this test with reference to ISO 6252:1992 (E), with the notch according to ASTM 1473, in the following way:

[0076] The CTL test is a test for accelerated slow crack growth where the acceleration is maintained by elevated temperature of 60 °C. The testing is performed in a surface active solution and the incorporation of a notch both accelerates the time to failure and ensures a plain strain in the samples.

[0077] The stress in the samples was 5.0 MPa (actual stress in the notched region). The surfactant used in the test was IGEPAL CO-730 at a temperature of 60 °C.

[0078] The samples are prepared by pressing a plaque with a total length of 125 to 130 mm and a width at its ends of 21 ± 0.5 mm. The plaque then is milled into the correct dimensions in a fixture on two of the sides with a centre distance of both holders of 90 mm and a hole diameter of 10 mm. The central part of the plaque has a parallel length of 30 ± 0.5 mm, a width of 9 ± 0.5 mm, and a thickness of 6 ± 0.5 mm.

[0079] A front notch of 2.5 mm depth is then cut into the sample with a razor blade fitted into a notching machine (PENT-NOTCHER, Norman Brown engineering), the notching speed is 0.2 mm/min. On the two remaining sides side grooves of 0.8 mm are cut which should be coplanar with the notch. After making the notches, the sample is conditioned in 23 ± 1 °C and 50 % relative humidity for at least 48 h. The samples are then mounted into a test chamber in which the active solution (10 % water solution IGEPAL CO-730, chemical substance: 2-(4-Nonyl-phenoxy)ethanol, $C_{17}H_{28}O_2$) is kept. The samples are loaded with a dead weight and at the moment of breakage an automatic timer is shut off.

g) Pressure testing and design stress

[0080] The design stress rating is the circumferential stress a pipe is designed to withstand for 50 years without failure and is determined for different temperatures in terms of the Minimum Required Strength (MRS) according to ISO/TR 9080. Thus, MRS 8.0 means that the pipe is a pipe withstanding a hoop stress of 8.0 MPa gauge for 50 years at 20 °C.

[0081] These values are calculated from the results of the pressure testing which are carried out according to ISO 1167. Pipes with a diameter of 32 mm are tested at different temperatures and inner pressure.

h) Flexural modulus

[0082] Flexural modulus was determined according to ISO 178. The test specimens were 80 x 10 x 4.0 mm (length x width x thickness). The length of the span between the supports was 64 mm, the test speed was 2 mm/min and the loadcell was 100 N. The equipment used was an Alwetron TCT 25.

2. Polyethylene compositions

[0083] Production of polyethylene composition base resins was performed in a multistage reaction comprising a pre-polymerisation in slurry in a 50 dm^3 loop reactor, followed by transferring the slurry to a 500 dm^3 loop reactor wherein polymerisation was continued in slurry to produce the low molecular weight component, and a second polymerisation in a gas phase reactor in the presence of the product from the second loop reactor to produce the comonomer containing high molecular weight component. The comonomer was 1-butene in all compositions produced.

[0084] As a catalyst, Lynx 200 from Engelhard Corporation in Pasadena, USA, was used.

[0085] For the comparative examples, a Ziegler-Natta catalyst in accordance with Example 1 of EP 0 688 794 has been used.

[0086] The nucleating agent used in the Examples is Pigment Cromophtal blue 4GNP (phtalocyanine blue).

[0087] The polymerisation conditions applied are listed in Table 1.

[0088] Examples 1 and 2, showing compositions 1 and 2, respectively, are Examples according to the invention. Example 3 is a comparative Example which shows composition 3. This is a polyethylene composition according to the prior art. In all three Examples in the step of prepolymerization homopolymers are produced.

Table 1:

Example	1	2	3 (Comp.)
Prepolymerisation			

(continued)

Example		1	2	3 (Comp.)
Temperature	°C	60	60	60
Pressure	bar	62	63	63
MFR_5	g/10 min	5	7	0.5
Slurry Polymerisation in Loop Reactor				
Temperature	°C	85	95	95
Pressure	bar	57	58	58
C_2 concentration	mol%	4.0	4.0	5.6
H_2/C_2	mol/kmol	217.6	277.0	947
C_4/C_2	mol/kmol	50.0	0.0	0.0
MFR_2	g/10 min	52	47	442
Density	kg/m^3	962	975	975
Gas Phase Polymerisation				
Temperature	°C	85.0	85.0	85.0
Pressure	bar	20	20	20
H_2/C_2	mol/kmol	28	28	48
C_4/C_2	mol/kmol	194	171	218
JSW CIM90P Extruder				
Feed	kg/h	221	221	221
SEI	kWh/t	329	291	280
Melt temperature	°C	217	226	226
Properties of Base resin				
Density	kg/m^3	933	936	941
Split (Prepol./loop/gas	phase)	2 : 38 : 60	2 : 38 : 60	2 : 44 : 54
Properties of Composition				
MFR_5	g/10 min	0.43	0.41	0.91
MFR_{21}	g/10 min	8.4	8.1	25.2
Density	kg/m^3	935	939	951
Comonomer content	wt%	3.75	3.11	2.85
Flexural modulus	MPa	614	674	880*
$T_{crit.}$ (RCP-S4)	°C	-10	-8	-4
$SHI_{2.7/210}$		24.9	23.4	33.1
$\eta_{2.7\ \kappa\Pi\alpha}$	kPas	106	113	52
$\eta_{747\ \Pi\alpha}$	kPas	160.3	172.7	85.7
Pressure testing (80 °C, 4.6 MPa)	h	> 845	> 700	> 400
MRS	MPa	≥ 8.0	≥ 8.0	8.74
CTL	h	> 1500	> 1500	> 5000
Notch test	h	> 1000	> 1000	> 5000
Cromophtal blue 4GNP	wt%	0.1	0.1	0
Carbon black	wt%	0	0	2.3

* without Carbon black

Claims

1. A pipe comprising a polyethylene composition comprising a base resin which comprises

(a) an ethylene homo- or copolymer fraction (A); and
(b) an ethylene homo- or copolymer fraction (B),

wherein

(i) fraction (A) has a lower weight average molecular weight than fraction (B);
(ii) the base resin has a density of 932 to 938 kg/m^3, determined according to ISO 1183-2;
(iii) the polyethylene composition has an MFR_5 of 0.1 to 0.6 g/10 min, determined according to ISO 1133; and
(iv) the polyethylene composition has a shear stress $\eta_{2.7}$ kPa (viscosity at a shear stress of 2.7 kPa at 190°C) of 85 to 230 kPas.

2. The pipe according to claim 1, wherein the polyethylene composition further comprises a nucleating agent.

3. The pipe according to any one of the preceding claims, wherein fraction (A) has a MFR_2 of 10 to 400 g/10 min, determined according to ISO 1133.

4. The pipe according to claim 3, wherein fraction (A) has an MFR_2 of 25 to 100 g/10 min, determined according to ISO 1133.

5. The pipe according to any one of the preceding claims, wherein fraction (A) has a density of 960 to 980 kg/m^3, determined according to ISO 1183-2.

6. The pipe according to any one of the preceding claims, wherein the $SHI_{(2.7/210)}$ (ratio of the viscosity, measured at a shear stress of 2.7 kPa and 210kPa at 190°C) of the polyethylene composition is 10 to 49.

7. The pipe according to any one of the preceding claims, wherein the flexural modulus of the polyethylene composition is 300 to 700 MPa, determined according to ISO 178.

8. The pipe according to any one of the preceding claims, wherein the weight split between fraction (A) and fraction (B) is (30-47) : (70-53).

9. The pipe according to any of the preceding claims wherein the rapid crack propagation resistance of the pipe made of the polyethylene composition as measured in the S4 test according to ISO 13477:1997 results in a T_{crit} of < -6 °C.

10. The pipe according to any of the preceding claims wherein the slow crack propagation resistance of the pipe made of the polyethylene composition as measured according to ISO 13479:1997 is > 500 h.

11. The pipe according to any of the preceding claims wherein the base resin comprises 0.2 to 3.0 mol% of at least one alpha-olefin comonomer.

12. The pipe according to any of the preceding claims wherein fraction (B) comprises 0.4 to 6.0 mol% of at least one alpha-olefin comonomer.

13. The pipe according to any of the preceding claims which fulfils the MRS 8.0 requirement according to ISO 9080.

14. Use of a polyethylene composition comprising a base resin which comprises

(a) an ethylene homo- or copolymer fraction (A); and
(b) an ethylene homo- or copolymer fraction (B),

wherein

(i) fraction (A) has a lower weight average molecular weight than fraction (B);
(ii) the base resin has a density of 932 to 938 kg/m^3, determined according to ISO 1183-2;
(iii) the polyethylene composition has an MFR_5 of 0.1 to 0.6 g/10 min, determined according to ISO 1133; and
(iii) the polyethylene composition has a shear stress $\eta_{2.7}$ kPa (viscosity at a shear stress of 2.7 kPa at 190°C) of 85 to 230 kPas.

for the production of a pipe.

15. The use according to claim 14, wherein the polyethylene composition further comprises a nucleating agent.

16. The use according to any one of claims 14 to 15, wherein fraction (A) has a MFR_2 of 10 to 400 g/10 min, determined according to ISO 1133.

17. The use according to claim 16, wherein fraction (A) has an MFR_2 of 25 to 100 g/10 min, determined according to ISO 1133.

18. The use according to any one of claims 14 to 17, wherein fraction (A) has a density of 960 to 980 kg/m^3, determined according to ISO 1183-2.

19. The use according to any one of claims 14 to 18, wherein the $SHI_{(2.7/210)}$ (ratio of the viscosity, measured at a shear stress of 2.7 kPa and 210kPa at 190°C) of the polyethylene composition is 10 to 49.

20. The use according to any one of claims 14 to 19, wherein the flexural modulus of the polyethylene composition is 300 to 700 MPa, determined according to ISO 178.

21. The use according to any one of claims 14 to 20, wherein the weight split between fraction (A) and fraction (B) is (30-47) : (70-53).

22. The use according to any of claims 14 to 21, wherein the rapid crack propagation resistance of a pipe made of the polyethylene composition as measured in the S4 test according to ISO 13477:1997 results in a T_{crit} of < -6 °C.

23. The use according to any of claims 14 to 22, wherein the slow crack propagation resistance of a pipe made of the polyethylene composition as measured according to ISO 13479:1997 is > 500 h.

24. The use according to any of claims 14 to 23, wherein the base resin comprises 0.2 to 3.0 mol% of at least one alpha-olefin comonomer.

25. The use according to any of claims 14 to 24 wherein fraction (B) comprises 0.4 to 6.0 mol% of at least one alpha-olefin comonomer.

Patentansprüche

1. Rohr, das eine Polyethylenzusammensetzung aufweist, umfassend ein Grundharz, das folgendes aufweist:

   (a) einen Anteil (A) aus einem Ethylenhomo- oder -copolymer; und
   (b) einen Anteil (B) aus einem Ethylenhomo- oder -copolymer,

   wobei

   (i) der Anteil (A) ein geringeres Gewichtsmittel des Molekulargewichts als der Anteil (B) aufweist;
   (ii) das Grundharz eine Dichte von 932 bis 938 kg/m^3 aufweist, und zwar gemäß ISO 1183-2 bestimmt;
   (iii) die Polyethylenzusammensetzung einen MFR_5-Wert von 0,1 bis 0,6 g/10 min aufweist, und zwar gemäß ISO 1133 bestimmt; und
   (iv) die Polyethylenzusammensetzung eine Scherbeanspruchung $\eta_{2,7\ kPa}$ (Viskosität bei einer Scherbeanspruchung von 2,7 kPa bei 190°C) von 85 bis 230 kPa•s aufweist.

2. Rohr nach Anspruch 1, wobei die Polyethylenzusammensetzung ferner einen Keimbildner aufweist.

3. Rohr nach einem der vorstehenden Ansprüche, wobei der Anteil (A) einen MFR_2-Wert von 10 bis 400 g/10 min aufweist, und zwar gemäß ISO 1133 bestimmt.

4. Rohr nach Anspruch 3, wobei der Anteil (A) einen MFR_2-Wert von 25 bis 100 g/10 min aufweist, und zwar gemäß ISO 1133 bestimmt.

5. Rohr nach einem der vorstehenden Ansprüche, wobei der Anteil (A) eine Dichte von 960 bis 980 kg/m^3 aufweist, und zwar gemäß ISO 1183-2 bestimmt.

6. Rohr nach einem der vorstehenden Ansprüche, wobei der Wert $SHI_{(2,7/210)}$ (Viskositätsverhältnis, bei einer Scherbeanspruchung von 2,7 kPa und 210 kPa bei 190°C gemessen) der Polyethylenzusammensetzung 10 bis 49 beträgt.

7. Rohr nach einem der vorstehenden Ansprüche, wobei der Biegemodul der Polyethylenzusammensetzung 300 bis 700 MPa beträgt, und zwar gemäß ISO 178 bestimmt.

8. Rohr nach einem der vorstehenden Ansprüche, wobei die Aufteilung des Gewichts zwischen dem Anteil (A) und dem Anteil (B) (30 - 47) : (70 - 53) beträgt.

9. Rohr nach einem der vorstehenden Ansprüche, wobei die Beständigkeit gegenüber der schnellen Rißausbreitung eines Rohrs, das aus der Polyethylenzusammensetzung hergestellt ist, und zwar beim S4-Test gemäß ISO 13477: 1997 gemessen, einen T_{crit}-Wert von < -6°C ergibt.

10. Rohr nach einem der vorstehenden Ansprüche, wobei die Beständigkeit gegenüber der langsamen Rißausbreitung eines Rohrs, das aus der Polyethylenzusammensetzung hergestellt ist, und zwar gemäß ISO 13479:1997 gemessen, > 500 h beträgt.

11. Rohr nach einem der vorstehenden Ansprüche, wobei das Grundharz 0,2 bis 3,0 Mol-% von zumindest einem α-Olefin-Comonomer umfaßt.

12. Rohr nach einem der vorstehenden Ansprüche, wobei der Anteil (B) 0,4 bis 6,0 Mol-% von zumindest einem α-Olefin-Comonomer umfaßt.

13. Rohr nach einem der vorstehenden Ansprüche, das die Anforderung MRS 8.0 gemäß ISO 9080 erfüllt.

14. Verwendung einer Polyethylenzusammensetzung, die ein Grundharz aufweist, das folgendes aufweist:

    (a) einen Anteil (A) aus einem Ethylenhomo- oder -copolymer; und
    (b) einen Anteil (B) aus einem Ethylenhomo- oder -copolymer,

    wobei

    (i) der Anteil (A) ein geringeres Gewichtsmittel des Molekulargewichts als der Anteil (B) aufweist;
    (ii) das Grundharz eine Dichte von 932 bis 938 kg/m^3 aufweist, und zwar gemäß ISO 1183-2 bestimmt;
    (iii) die Polyethylenzusammensetzung einen MFR_5-Wert von 0,1 bis 0,6 g/10 min aufweist, und zwar gemäß ISO 1133 bestimmt; und
    (iv) die Polyethylenzusammensetzung eine Scherbeanspruchung $\eta_{2,7\ kPa}$ (Viskosität bei einer Scherbeanspruchung von 2,7 kPa bei 190°C) von 85 bis 230 kPa•s aufweist,

    für die Herstellung eines Rohrs.

15. Verwendung nach Anspruch 14, wobei die Polyethylenzusammensetzung ferner einen Keimbildner aufweist.

16. Verwendung nach einem der Ansprüche 14 bis 15, wobei der Anteil (A) einen MFR_2-Wert von 10 bis 400 g/10 min aufweist, und zwar gemäß ISO 1133 bestimmt.

17. Verwendung nach Anspruch 16, wobei der Anteil (A) einen MFR_2-Wert von 25 bis 100 g/10 min aufweist, und zwar gemäß ISO 1133 bestimmt.

18. Verwendung nach einem der Ansprüche 14 bis 17, wobei der Anteil (A) eine Dichte von 960 bis 980 kg/m^3 aufweist, und zwar gemäß ISO 1183-2 bestimmt.

19. Verwendung nach einem der Ansprüche 14 bis 18, wobei der Wert $SHI_{(2,7/210)}$ (Viskositätsverhältnis, bei einer Scherbeanspruchung von 2,7 kPa und 210 kPa bei 190°C gemessen) der Polyethylenzusammensetzung 10 bis 49 beträgt.

20. Verwendung nach einem der Ansprüche 14 bis 19, wobei der Biegemodul der Polyethylenzusammensetzung 300 bis 700 MPa beträgt, und zwar gemäß ISO 178 bestimmt.

21. Verwendung nach einem der Ansprüche 14 bis 20, wobei die Aufteilung des Gewichts zwischen dem Anteil (A) und dem Anteil (B) (30 - 47) : (70 - 53) beträgt.

22. Verwendung nach einem der Ansprüche 14 bis 21, wobei die Beständigkeit gegenüber der schnellen Rißausbreitung eines Rohrs, das aus der Polyethylenzusammensetzung hergestellt ist, und zwar beim S4-Test gemäß ISO 13477: 1997 gemessen, einen T_{crit}-Wert von < -6°C ergibt.

23. Verwendung nach einem der Ansprüche 14 bis 22, wobei die Beständigkeit gegenüber der langsamen Rißausbreitung eines Rohrs, das aus der Polyethylenzusammensetzung hergestellt ist, und zwar gemäß ISO 13479:1997 gemessen, > 500 h beträgt.

24. Verwendung nach einem der Ansprüche 14 bis 23, wobei das Grundharz 0,2 bis 3,0 Mol-% von zumindest einem α-Olefin-Comonomer umfaßt.

25. Verwendung nach einem der Ansprüche 14 bis 24, wobei der Anteil (B) 0,4 bis 6,0 Mol-% von zumindest einem α-Olefin-Comonomer umfaßt.

Revendications

1. Tube comprenant une composition de polyéthylène comprenant une résine de base qui comprend

(a) une fraction d'homo- ou de copolymère d'éthylène (A) ; et
(b) une fraction d'homo- ou de copolymère d'éthylène (B),

dans lequel

(i) la fraction (A) possède un poids moléculaire moyen en poids inférieur à celui de la fraction (B) ;
(ii) la résine de base possède une masse volumique allant de 932 à 938 kg/m^3 déterminée selon la norme ISO 1183-2 ;
(iii) la composition de polyéthylène possède un MFR_5 allant de 0,1 à 0,6 g/10 min déterminé selon la norme ISO 1133 ; et
(iv) la composition de polyéthylène possède une contrainte de cisaillement $\eta_{2,7\ kPa}$ (viscosité à une contrainte de cisaillement de 2,7 kPa à 190 °C) allant de 85 à 230 kPas.

2. Tube selon la revendication 1, dans lequel la composition de polyéthylène comprend en outre un agent nucléant.

3. Tube selon l'une quelconque des revendications précédentes, dans lequel la fraction (A) possède un MFR_2 allant de 10 à 400 g/10 min déterminé selon la norme ISO 1133.

4. Tube selon la revendication 3, dans lequel la fraction (A) possède un MFR_2 allant de 25 à 100 g/10 min. déterminé selon la norme ISO 1133.

5. Tube selon l'une quelconque des revendications précédentes, dans lequel la fraction (A) possède une masse volumique allant de 960 à 980 kg/m^3 déterminée selon la norme ISO 1183-2.

6. Tube selon l'une quelconque des revendications précédentes, dans lequel le $SHI_{(2,7/210)}$ (rapport de la viscosité mesuré à une contrainte de cisaillement de 2,7 kPa et de 210 kPa à 190 °C) de la composition de polyéthylène va de 10 à 49.

7. Tube selon l'une quelconque des revendications précédentes, dans lequel le module de flexion de la composition de polyéthylène va de 300 à 700 MPa déterminé selon la norme ISO 178.

8. Tube selon l'une quelconque des revendications précédentes, dans lequel la séparation pondérale entre la fraction (A) et la fraction (B) est de (30-47)/(70-53).

9. Tube selon l'une quelconque des revendications précédentes, dans lequel la résistance à la propagation de fissure rapide du tube fabriqué avec la composition de polyéthylène, telle que mesurée dans l'essai S4 selon la norme ISO

13477:1997, donne une T_{crit} < -6 °C.

10. Tube selon l'une quelconque des revendications précédentes, dans lequel la résistance à la propagation de fissure lente du tube fabriqué avec la composition de polyéthylène, telle que mesurée selon la norme ISO 13479:1997 est > 500 h.

11. Tube selon l'une quelconque des revendications précédentes, dans lequel la résine de base comprend de 0,2 à 3,0 % en mole d'au moins un comonomère d'alpha-oléfine.

12. Tube selon l'une quelconque des revendications précédentes, dans lequel la fraction (B) comprend de 0,4 à 6,0 % en mole d'au moins un comonomère d'alpha-oléfine.

13. Tube selon l'une quelconque des revendications précédentes qui répond à l'exigence de MRS 8,0 selon la norme ISO 9080.

14. Utilisation d'une composition de polyéthylène comprenant une résine de base qui comprend

(a) une fraction d'homo- ou de copolymère d'éthylène (A) ; et
(b) une fraction d'homo- ou de copolymère d'éthylène (B),

dans laquelle

(i) la fraction (A) possède un poids moléculaire moyen en poids inférieur à celui de la fraction (B) ;
(ii) la résine de base possède une masse volumique allant de 932 à 938 kg/m^3 déterminée selon la norme ISO 1183-2 ;
(iii) la composition de polyéthylène possède un MFR_5 allant de 0,1 à 0,6 g/10 min. déterminé selon la norme ISO 1133 ; et
(iv) la composition de polyéthylène possède une contrainte de cisaillement $\eta_{2,7\ kPa}$(viscosité à une contrainte de cisaillement de 2,7 kPa à 190 °C) allant de 85 à 230 kPas,

pour la production d'un tube.

15. Utilisation selon la revendication 14, dans laquelle la composition de polyéthylène comprend en outre un agent nucléant.

16. Utilisation selon l'une quelconque des revendications 14 à 15, dans laquelle la fraction (A) possède un MFR_2 allant de 10 à 400 g/10 min. déterminé selon la norme ISO 1133.

17. Utilisation selon la revendication 16, dans laquelle la fraction (A) possède un MFR_2 allant de 25 à 100 g/10 min. déterminé selon la norme ISO 1133.

18. Utilisation selon l'une quelconque des revendications 14 à 17, dans laquelle la fraction (A) possède une masse volumique allant de 960 à 980 kg/m^3 déterminée selon la norme ISO 1183-2.

19. Utilisation selon l'une quelconque des revendications 14 à 18, dans laquelle le $SHI_{(2,7/210)}$ (rapport de la viscosité mesuré à une contrainte de cisaillement de 2,7 kPa et de 210 kPa à 190 °C) de la composition de polyéthylène va de 10 à 49.

20. Utilisation selon l'une quelconque des revendications 14 à 19, dans laquelle le module de flexion de la composition de polyéthylène va de 300 à 700 MPa déterminé selon la norme ISO 178.

21. Utilisation selon l'une quelconque des revendications 14 à 20, dans laquelle la séparation pondérale entre la fraction (A) et la fraction (B) est de (30-47)/(70-53).

22. Utilisation selon l'une quelconque des revendications 14 à 21, dans laquelle la résistance à la propagation de fissure rapide du tube fabriqué avec la composition de polyéthylène, telle que mesurée dans l'essai S4 selon la norme ISO 13477:1997, donne une T_{crit} < -6 °C.

23. Utilisation selon l'une quelconque des revendications 14 à 22, dans laquelle la résistance à la propagation de fissure lente du tube fabriqué avec la composition de polyéthylène, telle que mesurée selon la norme ISO 13479:1997 est > 500 h.

24. Utilisation selon l'une quelconque des revendications 14 à 23, dans laquelle la résine de base comprend de 0,2 à 3,0 % en mole d'au moins un comonomère d'alpha-oléfine.

25. Utilisation selon l'une quelconque des revendications 14 à 24, dans laquelle la fraction (B) comprend de 0,4 à 6,0 % en mole d'au moins un comonomère d'alpha-oléfine.

REFERENCES CITED IN THE DESCRIPTION

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